

Final Report AFOSR Grant # FA9550-05-1-0116 – Michael D. Fayer
Ultrafast Multidimensional Infrared Vibrational Echo Spectroscopy of Gases and Liquids

During the grant period 01/12/2004 - 30/11/2007, we have made major advances in applying ultrafast 2D IR vibrational echo spectroscopy to explicating important molecular dynamics problems and in developing the technique. The research performed can be roughly divided into two phases. In the early part of the grant period, we performed a comprehensive set of experiments that were initiated in conjunction with the instrument and methodology development. These experiments studied hydrogen bond dynamics, particularly of water. This work combined with theoretical collaborations helped define the current knowledge of hydrogen bond network structural evolution in water. The experiments involved the first use of ultrafast 2D IR heterodyne detected vibrational echo experiments with full phase information to extract dynamical information through the observation of the time evolution of the 2D vibrational echo spectral line shapes. Following the work on water, we developed a new approach for studying chemical dynamics under thermal equilibrium condition using 2D vibrational echo chemical exchange spectroscopy. The chemical exchange spectroscopy was used to study organic solute-solvent complexes by directly measuring complex formation and dissociation, and to make the first measurements of fast molecular isomerization around a carbon-carbon single bond in solution at room temperature for a system with a low barrier height comparable to ethane.

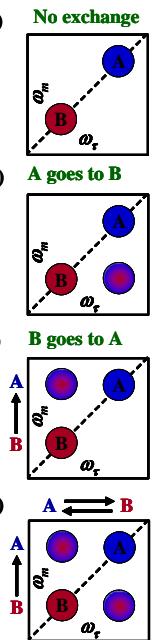
In the following the results will be briefly summarized. The most recent work using chemical exchange spectroscopy will be described first followed by a discussion of the work on water.

A. 2D Vibrational Echo Chemical Exchange Spectroscopy

1. The Effect of Chemical Exchange on the 2D Spectrum

Figure 1 illustrates schematically the influence of chemical exchange on the 2D vibrational echo spectrum. Two species, A and B, with vibrational transition frequencies, ω_A and ω_B , are in thermal equilibrium. Species A is converting to species B, and vice versa, but there is no net change in the populations of A and B because the rate of A's going to B's equals the rate of B's going to A's. Panel a shows the 2D spectrum at very short time prior to chemical exchange. There are two peaks on the diagonal, one for species A and one for species B with frequencies on both the ω_r and ω_m axes of ω_A and ω_B . Panel b shows what would happen if some of the A's convert to B's during the time period, T_w , between the second and third pulses in the vibrational echo pulse sequence. The first pulse produces a coherence between the states of species A at frequency ω_A . After time τ , the second pulse produces a population. There are several pathways, and a population can be produced in either the ground state (0) or the first excited state (1). During the period T_w , some A's turn into B's ($A \rightarrow B$). The third pulse again produces a coherence, but it is a coherence of species B at ω_B , followed by echo emission at ω_B . Because the first interaction (frequency on the ω_r axis) is at ω_A but the last interaction and echo emission (frequency on the ω_m axis) is at ω_B , an off-diagonal peak is generated as shown in panel b. Panel c shows what happens if B's turn into A's ($B \rightarrow A$). Everything is equivalent to the description of panel b, but the initial frequency is ω_B and the final frequency is ω_A .

Figure 1 . In a real system, the number of A's turning into B's in a given time period is equal to the number of B's turning into A's. As shown in panel d, the result is to



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14. ABSTRACT Ultrafast infrared 2D-IR vibrational echo experiments were extended experimentally and theoretically. Detailed studies of water dynamics were performed and compared to MD simulations. 2D-IR vibrational echo chemical exchange experiments were used to study the formation and dissociation kinetics of eight solute-solvent complexes, and the results were related to the enthalpies of formation. MD simulations of the chemical exchange were performed for the phenol-benzene complex and found to be in good agreement with the data. Chemical exchange experiments were used to measure the rate of gauche-trans orientational isomerization about a carbon-carbon single bond. The dynamics of molecules in the first solvation shell of solutes in mixed solvents were studied, and the time dependent solvent compositional fluctuations about solutes were elucidated. A detailed time dependent diagrammatic perturbation theory of the 2D-IR vibrational echo chemical exchange experiment including spectral diffusion, orientational relaxation, and vibrational relaxation was developed. An important new theoretical method for determining the dynamics from 2D-IR vibrational echo experiments was developed and demonstrated.						
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produce two off-diagonal peaks. Because some A's and B's may not have undergone chemical exchange, or may have undergone chemical exchange but reverted back to the original species prior to the third pulse, there are also diagonal peaks. The model spectrum in panel d is the spectrum for a time long compared to the chemical exchange time, while the spectrum in panel a is for a time short compared to the chemical exchange time. The rate of chemical exchange can be determined by observing the growth of the off-diagonal peaks in the 2D vibrational echo spectrum.

2. Organic Solute-Solvent Complex Formation and Dissociation

Solute and solvent molecules have anisotropic intermolecular interactions that can give rise to well-defined solute-solvent complexes. For organic solute-solvent systems, intermolecular interactions are generally relatively weak, a few kcal/mol. Such weak interactions will produce solute-solvent complexes that are short lived. Although short lived, the dissociation and formation of organic solute-solvent complexes can influence chemical processes such as reactivity.

Organic solute-solvent complexes are in equilibrium between the complex form and the free solute form. Because formation and dissociation occurs on a ps time scale, until recently it has not been possible to observe the chemical exchange process between the two forms of the solute. Using vibrational echo chemical exchange spectroscopy we have studied a number of systems. The phenol-benzene complex is used as an example. Figure 2a displays the spectrum of the hydroxyl OD stretch of phenol in a mixed solvent of benzene (20 mol%) and CCl_4 (80 mol%). The high frequency peak is the free phenol, and the low frequency peak is the phenol-benzene complex. The structure of the complex, determined from electronic structure calculations, is shown in the figure. The species are in equilibrium, with complexes constantly dissociating and free phenols associating with benzene to form complexes. Panel b shows the 2D vibrational echo spectrum at short time, $T_w = 200$ fs; no significant exchange has occurred. At short time, the two species give two peaks on the diagonal, which correspond to the 2 peaks in the absorption spectrum. At long time, 14 ps, extensive chemical exchange has occurred. Off-diagonal peaks have grown in as can be seen clearly in panel c. The two peaks correspond to complex dissociation and formation. Panel c has the appearance of the schematic shown in figure 1d, and the discussion surrounding the origins of the off-diagonal peaks in figure 1 applies to the experimental data shown in figure 2.

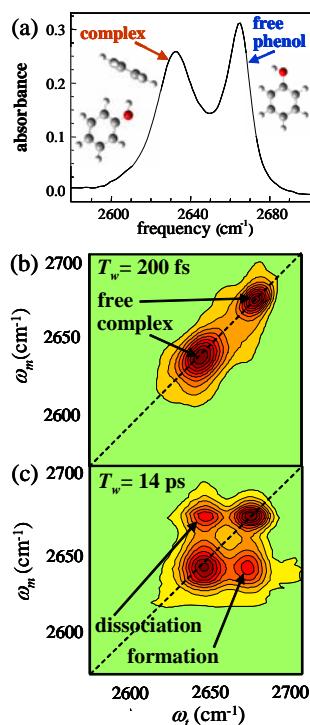


Figure 2
dissociation is equal to the rate of complex formation, we can fit everything using a *single adjustable parameter*, the complex dissociation time, $\tau_d = 1/k_{cf}$, where k_{cf} is the rate constant for dissociation of the complex (c) to the free form (f).

Figure 3 displays the data and fits for the chemical exchange dynamics of the phenol-benzene complex. There are four peaks in the 2D vibrational echo spectra, the two diagonal

The growth of the off-diagonal peaks with increasing T_w can be used to directly determine the thermal equilibrium rate for complex formation and dissociation. In addition to chemical exchange, there are other dynamical processes that contribute to the time dependent changes in the spectrum. These include vibrational lifetimes, orientational relaxation, etc. With the necessary input parameters all known, there is only one adjustable parameter to fit the T_w dependence of all of the peaks (two diagonal peaks and two off-diagonal peaks) in the spectra. Because the rate of complex

peaks for the complex (top points and curve) and free (second curve and points from top) species, and the two off-diagonal peaks (bottom points and curve) for $c \rightarrow f$, and $f \rightarrow c$. As can be seen from figure I.3, the data are fit very well with the single parameter τ_d . (The mathematical details used to fit the data have been presented.) The results of the fitting yields $\tau_d = 10$ ps.

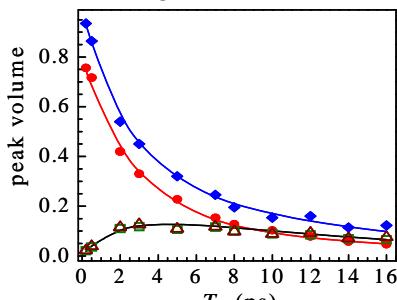


Figure 3

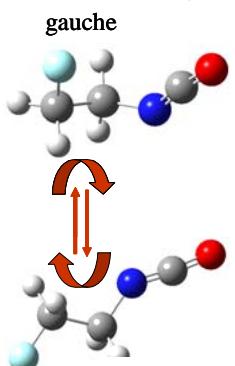
Eight complexes of phenol and phenol derivatives with benzene and benzene derivatives were investigated. The series of complexes have a wide range of hydrogen bond strengths. The measured dissociation times for the eight complexes range from 3 ps to 31 ps. The bond dissociation enthalpies (negative of the formation enthalpies) range from 0.6 kcal/mol to 2.5 kcal/mol. It was found that the hydrogen bond dissociation times, τ , are correlated with the dissociation enthalpies in a manner akin to an Arrhenius equation. The correlation can be qualitatively understood in terms of transition state theory.

In addition to the experiments, comprehensive quantum chemistry calculations and MD simulations have been conducted in collaboration with Professor Minhaeng Cho, Department of Chemistry and Center for Multidimensional Spectroscopy, Korea University, Seoul, Korea. The simulations are in good agreement with the experimental data and provide microscopic insights into the nature of the exchange process and solute-solvent complex interactions. These experimental and theoretical studies have provided the first detailed information on the dynamics of weakly hydrogen bonded organic species and the relationship between dynamics and strengths of the hydrogen bonds.

3. Isomerization Around a Carbon-Carbon Single Bond

Isomerization of organic molecules is responsible for the vast diversity of their chemical structures and the ability of both small molecules and large biological molecules to undergo structural changes without breaking chemical bonds. During the course of isomerization a molecule is transformed from one relatively stable conformation to another by passing through unfavorable configurations. Ethane and its derivatives are textbook examples of molecules that undergo this type of isomerization. The transition from one staggered state to another leaves ethane structurally identical. Therefore, the result of ethane isomerization cannot be observed through a change in chemical structure. In a 1,2-di-substituted ethane derivative, the molecule can undergo a similar isomerization. However, a 1,2-di-substituted ethane has two distinct staggered conformations, gauche and trans. Carbon-carbon bond isomerization has been the subject of intense theoretical and experimental study for more than 100 years.

The trans-gauche isomerization of 1,2-disubstituted ethane derivatives, e.g. n-butane, is one of the simplest cases of a first-order chemical reaction. This type of isomerization has



trans Figure 4

served as a basic model for modern chemical reaction kinetic theory and molecular dynamics (MD) simulation studies in condensed phases. In spite of extensive theoretical investigation, until this work no corresponding kinetic experiments have been performed to test the results, partially due to the low rotational energy barrier of the n-butane (~3.4 kcal/mol) and other simple 1,2-disubstituted ethane derivatives.

The 2D vibrational echo chemical exchange spectroscopic method has been applied to the study of the ultrafast trans-gauche isomerization dynamics of a simple 1,2-disubstituted ethane derivative, 1-fluoro-2-isocyanato-ethane, in a room temperature liquid. The gauche and trans forms of the molecule are shown in figure 4. The experiments were performed by observing the time dependence of the 2D spectrum of the isocyanate ($N=C=O$) group's antisymmetric stretching mode. In principle, the method for

determining the rate of isomerization is identical to the method employed for determining the rate of solute-solvent complex formation and dissociation discussed above. The gauche and trans forms show overlapping but resolvable antisymmetric stretch peaks in the linear absorption spectrum. However, the 2D vibrational echo spectrum has greater complexity because than the phenol-benzene solute solvent system because there is an addition peak in the linear spectrum resulting from an unassigned mode, possibly a overtone or combination band. This mode is coupled through anharmonic terms in the vibrational potential to the antisymmetric mode of interest. The coupling produces additional off-diagonal peaks. The nature of these peaks is well understood, and it was possible to observe the T_w dependent growth of the chemical exchange off-diagonal peaks.

Because of the coupling to the unassigned band, the details of the analysis of the data are more complex than for the solute-solvent complex chemical exchange problem. However, with independent measurements of the vibrational population dynamics and orientational relaxation rates using IR pump-probe experiments, there remained only one unknown parameter. The isomerization rate constant, $k_{TG} = k_{GT}$, was used in fitting the T_w dependent 2D vibrational echo data. The trans to gauche and gauche to trans rate constants are taken to be equal within experimental error because the equilibrium constant is 1.

Figure 5 shows the T_w dependent peak volume data (points) and the results of the fits (curves). The diagonal peaks for gauche (top curve and points) and trans (second curve and points) and the off-diagonal peaks (bottom curve and points) are all fit very well using the

isomerization rate constant as the only adjustable parameter. The fits yield $1/k_{TG} = 1/k_{GT} = 43 \pm 10$ ps.

Based on the experimental results for the 1-fluoro-2-isocyanato-ethane, it is possible to calculate approximately the gauche-trans isomerization rate of n-butane and the rotational isomerization rate of ethane under the same conditions used in this study (CCl_4 solution at room temperature, 297 K). It is interesting to obtain a number for n-butane because there have been a large number of theoretical calculations for the isomerization of this molecule. Using the calculated barriers

for 1-fluoro-2-isocyanato-ethane and for n-butane and the assumption that the prefactors are the same, a ~40 ps time constant for the n-butane trans to gauche isomerization time constant ($1/k_{TG}$) was calculated. This value is identical within error to the 43 ps time found for the n-butane isomerization in CCl_4 at 300 K from MD simulations. Other MD simulations gave isomerization rates in liquid n-butane at slightly lower temperatures: 52 ps (292 K), 57 ps (292 K), 50 ps (273 K) and 61 ps (<292 K). All of these values are reasonably close to the value obtained based on the experimental measurements of 1-fluoro-2-isocyanato-ethane. In the same manner, the isomerization time constant for ethane was found to be ~12 ps.

The vibrational echo chemical exchange spectroscopy of solute-solvent complexes was also used to address solutes that make both and intramolecular and intermolecular hydrogen bond. These solute-solvent complexes revealed a new type of 3-center hydrogen bond. The work also explained a variety of novel affects such as accidental vibrational degeneracies, and their manifestation in 2D vibrational echo spectra. Overall, the development of vibrational echo chemical exchange spectroscopy is an important advance that has already lead to unique observations of solute-solvent dynamics and molecular isomerization.

B. 2D Vibrational Echo Spectroscopy of Water

Water has profound effects on diverse fields of science including chemistry, materials science, and biology. The properties of liquid water are dominated by the hydrogen bonds among water molecules. The hydrogen bonds produce structured networks that are responsible

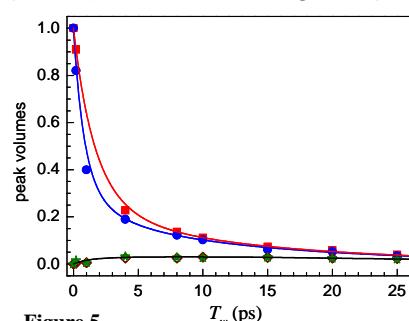


Figure 5

for water's unique properties. The water hydrogen bond network is constantly changing over a range of time scales. A water molecule can make zero to four hydrogen bonds that are constantly becoming shorter (stronger) and longer (weaker), formed and broken. The constantly changing hydrogen bond networks permit water to accommodate a wide array of chemical processes such as ion hydration and protein folding.

Ultrafast 2D IR vibrational echoes were used to investigate hydrogen bond network dynamics in water. In collaboration with Professor James L. Skinner, Department of Chemistry, University of Wisconsin at Madison, simulations were combined with the experimental results and calculations of the experimental observables to produce a detailed picture of water dynamics. The connection between hydrogen bond network dynamics and the experiments is through the frequency of the hydroxyl stretch. The frequency of the hydroxyl stretch is lowered (red shifted) when water makes a hydrogen bond. Stronger and more hydrogen bonds cause a greater red shift of the hydroxyl oscillator frequency than weaker and fewer hydrogen bonds. As the hydrogen bond network evolves in time, the strength and number of hydrogen bonds change, which in turn causes the water oscillators' frequencies to change. This is referred to as spectral diffusion.

To understand the relationship between the 2D vibrational echo spectrum and the hydrogen bond dynamics qualitatively, an analogy can be made to the chemical exchange experiments discussed in the last section. In the phenol-benzene complex system, at short time there are two peaks on the diagonal. At longer times, the off-diagonal peaks appear. In water, there are a vast number of hydrogen bonded structures. At short time, these structures give rise to an elongated band down the diagonal of the 2D spectrum. As time goes on, exchange of structures make "off-diagonal" peaks grow in. However, these are not resolved. Instead, on either side of the diagonal, effectively continuous groups of off-diagonal peaks grow in. The result is a change in shape of the short time elongated band to a more and more symmetrical band rather than the appearance of new peaks.

To obtain a more quantitative view, consider a single water molecule hydroxyl oscillator.

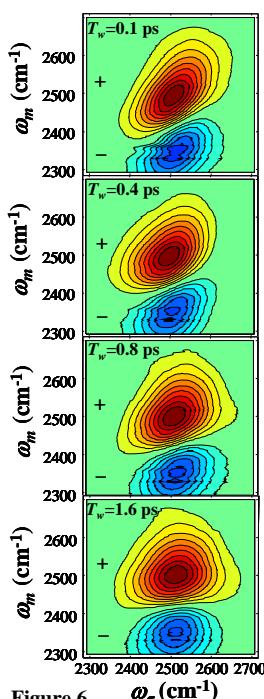


Figure 6

At $t = 0$, it will have a particular frequency, $\omega(0)$. As the local H-bond structure changes, the frequency will change. The time evolution of the frequency is referred to as spectral diffusion. At long time, independent of its starting frequency the oscillator can have any frequency in the entire broad hydroxyl stretch absorption spectrum because it has lost memory of its starting frequency (structure). A measure of the frequency evolution, and therefore the structural evolution, is the frequency-frequency correlation function (FFCF). The FFCF is related to the probability that an oscillator with initial frequency $\omega(0)$ still has the same frequency at time t later, averaged over all starting frequencies. Vibrational echo experiments make the FFCF an experimentally observable quantity. The FFCF is the basic input into time dependent diagrammatic perturbation theory that is used to calculate non-linear optical experimental observables in general and vibrational echo signals in particular. The FFCF and diagrammatic perturbation theory should provide an accurate description for systems such as phenol complexes. However, for water recent theoretical work has shown that it is necessary to go beyond diagrammatic perturbation theory because of non-Condon effects that influence experimental observables. Nonetheless, even for water, the FFCF provides important qualitative insights and an almost quantitative description of water dynamics.

The experiments and simulations look at the time evolution of the hydroxyl stretching frequency (the OD stretch of low concentration HOD in H_2O), which reports on the structural evolution of the water network. HOD is used to avoid vibrational excitation transfer, which

would influence the experiments and is not a ground state equilibrium process. Figure 6 displays 2D vibrational echo spectra of water as a function of T_w . The figure shows both the 0-1 (positive going) and the 1-2 (negative going) OD hydroxyl stretch transitions. Each contour represents a 10% change in signal. At 100 fs (top panel), The 0-1 band is substantially elongated along the diagonal. As time increases, the band changes shape and becomes increasingly symmetrical. By 1.6 ps, 0-1 band is basically symmetrical along the ω_r axis. It would be essentially round, but the overlap with the negative going 1-2 band eats away the bottom portion. The change in shape is directly related to the structural evolution of the hydrogen bond network. When the shape becomes symmetrical, all hydrogen bond structural configurations have been sampled, which happens by ~3 ps.

Data such as those presented in figure I.6 can be analyzed quantitatively. The experimental data are compared to results from simulations of water to determine the nature of the hydrogen bond network motions on different time scales. The results show that the shortest time scale fluctuations (< a few hundred femtoseconds) involve very local hydrogen bond motions mainly of the length of a hydrogen bond. The longer time scale dynamics are global hydrogen bond network rearrangements that lead to the complete randomization of the water structure. The 2D vibrational echo results determined this slowest component to be 1.5 ps. This is the time scale on which the water hydrogen bond network restructures to accommodate processes such as solvation or protein folding.

In addition to the vibrational echo experiments on water, pump-probe experiments were also employed to study hydrogen bond dynamics, and vibrational echoes were also employed to investigate hydrogen bond dynamics of methanol.